# The Effect of Transreactions on Phase Behavior in Poly(ethylene 2,6-naphthalate) and Poly(ethylene isophthalate) Blends

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ABSTRACT: The effect of transreactions on the phase behavior in poly(ethylene 2,6-naphthalate) and poly(ethylene isophthalate) blends was investigated by using differential scanning calorimetry. The transreactions between two polymers were confirmed by <sup>1</sup>H nuclear magnetic resonance. At the beginning step of transreactions, the blend samples show two glass transitions. However, after transreactions occur to some extent (i.e., when the degree of randomness is >0.4), a single glass transition is observed. As the transreactions proceed, the composition difference between ethylene 2,6-naphthalate-rich and ethylene isophthalate-rich phases lessens. Additionally, the weight fraction of each phase decreases because of the increment of interfacial fraction with the lapse of reaction time. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1851–1858, 1999

Keywords: transreactions; phase composition; degree of randomness; phase fraction

## INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN) is quite useful for packaging and engineering resin applications because of good mechanical, thermal, and gas barrier properties.<sup>1-4</sup> However, despite these good properties of PEN, there are some barriers for commercialization of PEN. Its monomer is expensive and its processing temperature is extremely high due to a combination of relatively high melting temperature  $(T_m)$  and high melt viscosity. Blending PEN with other polymers is an economical and rapid way to overcome these limitations. Recently, much work has been done on blends of PEN with other polyesters. These studies involve miscibility and properties of blends of PEN with poly(ethylene terephthalate) (PET),<sup>5-8</sup>

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polycarbonate (PC),<sup>9</sup> liquid crystalline polymer (LCP),<sup>10,11</sup> and poly(butylene 2,6-naphthalate) (PBN).<sup>12,13</sup> Guo<sup>14,15</sup> reported that PEN is immiscible with the other component polymers in PEN/PET, PEN/PC, and PEN/poly(ethylene isoterephthalate) (PEIT) blends. However, the miscibility of these polyester blends can be improved easily by the transreactions occurring between two component polymers.

Transreactions such as alcoholysis, acidolysis, and transesterification commonly occur at the melt state in polyester blends. It has been found by many investigators<sup>16–22</sup> that the transreactions in polyester blends can play an important role in their miscibility. Porter et al.<sup>23,24</sup> have reviewed in detail the relationship between the miscibility and transreactions in many polyester blends. Transreactions produce first block copolymers and finally random copolymers. These copolymers enhance the miscibility between components of blends. After sufficient transreactions

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Properties	PEN	PEI
$M_n^{\rm a}$ (g/mol)	20,300	45,400
$[\eta]^{\rm b}$ (dl/g)	0.51	0.78
$T_m$ (°C)	268.5	_
$T_g$ (°C)	121.7	61.5

 $\ensuremath{\text{PEN}}$  , poly(ethylene 2,6-naphthalate);  $\ensuremath{\text{PEI}}$  , poly(ethylene isophthalate).

<sup>a</sup> Determined by end group analysis.

<sup>b</sup> Measured in a mixed solvent of phenol/1,1,2,2-tetrachloroethane (60/40, w/w) at 25°C.

occur, one homogeneous phase showing a single glass transition is obtained in many polyester blends such as PEN/PET,<sup>8</sup> PET/PC,<sup>25</sup> and PET/ phenoxy<sup>26</sup> blends. Therefore, it is important in immiscible polyester blends to induce and control transreactions both for improving miscibility of blends and for obtaining new copolyesters.

In our previous article,<sup>8</sup> during the transition process from the heterogeneous phase to the homogeneous one by the transreactions in PEN/PET blends, the phase behavior was systematically investigated. It was suggested that the initial heterogeneous system becomes a single phase through diminishment in the composition difference between two coexisting phases, without large changes to the phase fractions. In the present study, the phase behavior of PEN/poly-(ethylene isophthalate) (PEI) blends as a function of the degree of transreactions has been examined. The results are also discussed in comparison with those of PEN/PET blends.

## **EXPERIMENTAL**

#### **Polymers**

PEN was supplied kindly by Kolon Industry (Korea) and PEI was synthesized in our laboratory.<sup>27</sup> The number-average molecular weight  $(M_n)$ , intrinsic viscosity  $(\eta)$ , and thermal properties for two polymers are listed in Table I.

#### **Blend Preparation**

The blends were prepared by dissolving the component polymers in a mixed solvent of phenol/ 1,1,2,2-tetrachloroethane (60/40, wt/wt). The polymer solutions were poured into a large excess of acetone. The precipitated polymers were filtered and then dried in a vacuum oven at 60°C for 24 h.

#### Transreactions

Heat treatment for transreactions was performed on a differential scanning calorimeter (DSC, Perkin-Elmer DSC-7). PEN/PEI (60/40, wt/wt) blend samples were held at three reaction temperatures (270, 285, and 300° C) for various reaction times ( $\approx$ 5–40 min). To obtain PEN/PEI copolymers, PEN/PEI blend samples for all the blend compositions were held at 285°C for 60 min. After heat treatment, the samples were quenched into liquid nitrogen.

#### Analysis

<sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained by using a Brüker AC 200 spectrometer (200 MHz) on solutions in trifluoroacetic acid/deuterated chloroform (1/5, v/v). Thermal analysis was performed on a Perkin-Elmer DSC-7 with a scanning rate of 20° C/min. The glass transition temperature ( $T_g$ ) was taken as the inflection point of the heat capacity change.

# **RESULTS AND DISCUSSION**

## **Confirmation of Transreactions**

Figure 1 shows <sup>1</sup>H NMR spectra in the range from 4.6 to 5.1 ppm, for PEN/PEI (60/40) blend samples with various reaction times at 285°C. Only the two peaks are observed at 4.90 and 4.80 ppm in the spectrum of the sample which was not heat treated. These two peaks correspond to proton signals of the ethylene unit in PEN and PEI homopolymers, respectively. For the samples heat treated at 285°C, a new peak appears at 4.85 ppm, and its intensity increases as a function of the reaction time. This peak is assigned to protons of the ethylene unit which is between one 2,6-naphthalate (N) and one isophthalate (I) unit, formed by transreactions.<sup>28</sup> Hence, the relative peak areas of the three signals at 4.90, 4.85, and 4.80 ppm are proportional to the concentrations of ethylene units between two 2,6-naphthalate units (NEN), between one 2,6-naphthalate and one isophthalate unit (NEI), and between two isophthalate units (IEI) in the reacted blend system, respectively.

Following a method similar to that of Yamadera and Murano,<sup>29</sup> the number-average se-



**Figure 1** <sup>1</sup>H NMR spectra of PEN/PEI (60/40) blend samples heat treated at 285°C for various time intervals.

quence lengths of 2,6-naphthalate unit  $(L_{n\rm N})$  and isophthalate unit  $(L_{n\rm I})$  can be found from integral intensities of three types of ethylene units. The probability  $(P_{\rm NI})$  of finding an I unit next to an N unit is:

$$P_{\rm NI} = \frac{A_{\rm NEI}/2}{A_{\rm NEI}/2 + A_{\rm NEN}} \tag{1}$$

similarly:

$$P_{\rm IN} = \frac{A_{\rm NEI}/2}{A_{\rm NEI}/2 + A_{\rm IEI}} \tag{2}$$

where  $A_{\text{NEN}}$ ,  $A_{\text{NEI}}$ , and  $A_{\text{IEI}}$  represent the relative integrated areas of NEN, NEI, and IEI peaks, respectively. Also, the number-average sequence lengths ( $L_{nN}$  and  $L_{nI}$ ) are given by:

$$L_{n\rm N} = \frac{1}{P_{\rm NI}} \tag{3}$$

$$L_{n\rm I} = \frac{1}{P_{\rm IN}} \tag{4}$$

Furthermore, the degree of randomness (B) is defined as the summation of the two probabilities:

$$B = P_{\rm NI} + P_{\rm IN} \tag{5}$$

For random copolyesters, *B* is unity. If *B* is 1, the units tend to cluster in blocks of each unit, and B = 0 in a homopolymer mixture, whereas if *B* is >1, the sequence length becomes shorter, and B = 2 in an alternative copolyester.

Figures 2 and 3 show the variations of the number-average sequence length of 2,6-naphthalate units and the degree of randomness with reaction time at three reaction temperatures. As the reaction proceeds,  $L_{nN}$  decreases more rapidly at the higher reaction temperature. Also, the same trend was observed for  $L_{nI}$ , even though not shown in this article. The degree of randomness increases with reaction time. For the higher reaction temperature, B more rapidly approaches to 1.0, indicative of the formation of random copolyesters. From these behaviors, it is obvious that



**Figure 2** Change of the number-average sequence length of the 2,6-naphthalate unit with reaction time at three temperatures for PEN/PEI (60/40) blend: ( $\bigcirc$ ) 270°C; ( $\bigtriangleup$ ) 285°C; ( $\square$ ) 300°C.



**Figure 3** Change of the degree of randomness with reaction time at three temperatures for PEN/PEI (60/40) blend: ( $\bigcirc$ ) 270°C; ( $\triangle$ ) 285°C; ( $\square$ ) 300°C.

the transreactions between PEN and PEI take place at the melt state, more vigorously at the higher temperature, and that the blend system becomes randomized as the transreactions progress.

#### **Phase Behavior**

Figure 4 shows the dependence of thermal transitions on blend composition for the blend samples quenched after melting at 270°C for 1 min. For all the blend compositions, two glass transitions are observed. The lower and upper  $T_g$  are similar to those of  $T_g$  for pure PEI and PEN, respectively. Additionally,  $T_m$  of PEN dose not significantly change for all the blend compositions. These results indicate that PEN is immiscible with PEI for all the blend compositions.

Figure 5 shows the DSC curves for PEN/PEI (60/40) blend samples, which were isothermally maintained for various time intervals at 270, 285, and 300°C. The heat of cold crystallization and melting peaks reduce with reaction time, respectively. In addition, the cold crystallization and melting peaks disappear within the shorter reaction time for the higher reaction temperature. These thermal behaviors suggest that crystallization of PEN is hindered, due to the disruption of the chain periodicity as a consequence of transreactions.

Within the shorter reaction time, the blends show two glass transitions, which approach closer with the increase of reaction time. The higher  $T_g$ is attributable to ethylene 2,6-naphthalate (EN)rich phase, and the lower to ethylene isophthalate (EI)-rich phase. After a single glass transition is observed,  $T_{\sigma}$  does not move and glass transition takes place within a more narrow temperature range with the increase of reaction time. This reflects that transreactions enhance miscibility. The effect of reaction time and temperature on the glass transition behavior for PEN/PEI (60/40) blend is shown in Figure 6. The higher the reaction temperature, the shorter the time necessary to show a single glass transition, because transreactions occur more vigorously at the higher temperature. In the early step of transreactions, the EN-rich phase coexists with the EI-rich one, and the composition of each phase varies with the degree of transreactions. The compositions of the above two phases can be estimated, if we know the  $T_g$  vs composition relationship for a single phase system. Hence,  $T_g$  were measured for the blend samples maintained at 285°C for 60 min. Among many equations describing the  $T_g$  vs composition relationship, the Fox<sup>30</sup> and Gordon-Taylor equations<sup>31</sup> were used to predict  $T_g$  as a function of composition.

Fox equation:

$$1/T_{g} = w_{1}/T_{g1}^{o} + w_{2}/T_{g2}^{o}$$
(6)



**Figure 4** Dependence of thermal transitions on the blend composition of PEN/PEI blends: ( $\bigcirc$ )  $T_m$ ; ( $\square$ )  $T_g$ .



Figure 5 DSC curves for PEN/PEI (60/40) blend samples heat treated for various time intervals at three temperatures: (a) 270°C; (b) 285°C; and (c) 300°C. The arrow indicates the position of  $T_g$ .

Gordon-Taylor equation:

$$T_{g} = \frac{w_{1}T_{g1}^{\circ} + kw_{2}T_{g2}^{\circ}}{w_{1} + kw_{2}}$$
(7)

where  $T_{gi}^{o}$  is the glass transition temperature of i homopolymer,  $w_i$  is the weight fraction of i com-

ponent, and k is an adjusting parameter. The EN and EI units are designated as 1 and 2, respectively. As shown in Figure 7, the  $T_g$  behavior is described better by the Gordon-Taylor equation with a k value of 0.58 than by the Fox equation. As shown in Figures 5 and 6, the  $T_g$  of a single phase formed by the transreactions is almost in-



**Figure 6** Change of the glass transition behavior with reaction time at three temperatures for PEN/PEI (60/40) blend: ( $\bigcirc$ ) 270°C; ( $\bigcirc$ ) 285°C; ( $\square$ ) 300°C.

variant with reaction time (or sequence lengths of N and I units). This means that the  $T_g$  of the PEN/PEI blend with no transreactions (if this blend forms a single phase) may be equal to that



**Figure 7** Glass transition temperature vs composition curves for PEN/PEI copolymers prepared by heat treating of PEN/PEI blends at 285°C for 60min: ( $\bigcirc$ ) experimental value; (--) Fox equation; ( $\longrightarrow$ ) Gordon-Taylor equation.



**Figure 8** Change of coexisting phase compositions with reaction time at 270°C for PEN/PEI (60/40) blend: ( $\bigcirc$ ) EN-rich phase; ( $\square$ ) EI-rich phase.

of the random copolymer. Therefore, the compositions of EN-rich and EI-rich phases can be estimated by the following equations:

$$w_{1U} = \frac{k(T_{g2}^{\circ} - T_{gU})}{(T_{gU} - T_{g1}^{\circ}) + k(T_{g2}^{\circ} - T_{gU})}$$
(8)

$$w_{1L} = \frac{k(T_{g2}^{o} - T_{gL})}{(T_{gL} - T_{g1}^{o}) + k(T_{g2}^{o} - T_{gL})}$$
(9)

where U and L correspond to the EN-rich phase and the EI-rich one, respectively. Figure 8 shows that the difference in composition between the EN- and EI-rich phases lessens with reaction time for the blend samples heat treated at 270°C. The weight fractions of EN in the EN- and EI-rich phases approach mutually closer as reaction time increases, and reach a value of 0.6, consistent with the overall blend composition. This result can be explained as follows. In the beginning step of transreactions, reactions must take place mainly at the interface between the EN- and EIrich phases, and produce block copolymers. In the second step, some block copolymers containing the EN unit as a major component perhaps penetrate into the EN-rich phase. Similarly, other block copolymers with the EI unit as a major component diffuse into the EI-rich phase. This partial miscibility results in reducing the differ-

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**Figure 9** Change of the glass transition behavior with the degree of randomness for PEN/PEI (60/40) blend samples heat treated at three temperatures: ( $\bigcirc$ ) 270°C; ( $\bigcirc$ ) 285°C; ( $\square$ )300°C.

ence of coexisting phase compositions, which finally induce a homogeneous phase. The extent of transreactions required for forming a single phase closely relates to the polymer-polymer interaction parameter  $(\chi_{i/i})$ . Block copolymers formed by the transreactions can diffuse more easily in case of a small polymer-polymer interaction parameter, and just a little transreaction can form a single phase. It has been reported that a single phase is observed when B is >0.2, for PEN/PET blend samples heat treated at 280°C  $(\chi_{\text{PEN/PET}} = 0.015).^{8}$  On the other hand, a single  $T_{g}$  reflecting homogeneous phase for PEN/PEI blend is observed when the degree of randomness is greater than  $\approx 0.4$ , irrespective of reaction temperature, as shown in Figure 9. Hence, it is considered that  $\chi_{\text{PEN/PEI}}$  may be greater than  $\chi_{\text{PEN/PET}}$ 

The fractions of two coexisting phases and interfacial zone can be estimated, if we know the heat capacity changes at  $T_g$  of the partially miscible blend  $(\Delta C_p \mathbf{s})$  and the pure homopolymers  $(\Delta C_p^{\circ} \mathbf{s}).^{8,32}$  Assuming that  $\Delta C_p \mathbf{s}$  vary linearly with mass fractions and  $\Delta C_p^{\circ} \mathbf{s}$ ,

$$\Delta C_{pU} = \Delta C_{p1}^{\circ}(m_{1U}/m_T) + \Delta C_{p2}^{\circ}(m_{2U}/m_T) \quad (10)$$

$$\Delta C_{pL} = \Delta C_{p1}^{\circ}(m_{1L}/m_T) + \Delta C_{p2}^{\circ}(m_{2L}/m_T) \quad (11)$$

where  $m_{iU}$  and  $m_{iL}$  are the masses of component i in the EN- and EI-rich phases, and  $m_T$  is the total mass of the system. From equations 8–11, the weight fractions of the EN-rich phase  $(w_L)$ , EI-rich phase  $(w_L)$ , and interfacial zone  $(w_I)$  are given by:

$$w_{U} = \frac{\Delta C_{pU} [(T_{gU} - T_{g1}^{\circ}) + k(T_{g2}^{\circ} - T_{gU})]}{\Delta C_{p2}^{\circ}(T_{gU} - T_{g1}^{\circ}) + k\Delta C_{p1}^{\circ}(T_{g2}^{\circ} - T_{gU})}$$
(12)

$$v_L = \frac{\Delta C_{pL} [(T_{gL} - T_{g1}^{\circ}) + k(T_{g2}^{\circ} - T_{gL})]}{\Delta C_{p2}^{\circ}(T_{gL} - T_{g1}^{\circ}) + k\Delta C_{p1}^{\circ}(T_{g2}^{\circ} - T_{gL})} \quad (13)$$

$$w_1 = 1 - w_U - w_L \tag{14}$$

Figure 10 shows the variation of weight fractions of two phases and the interfacial zone with the reaction time for PEN/PEI (60/40) blend samples heat treated at 270°C. The fractions of EN- and EI-rich phases tend to decrease as the reaction time increases, which results in the increment of interfacial fraction. It is reported that the change of phase fractions during the homogenization process is negligibly small for the PEN/PET blend.<sup>8</sup> This discrepancy between the PEN/PEI and PEN/ PET blends may be caused by the following reason. The copolymers formed by the transreactions in the PEN/PEI blend diffuse more slowly than those in the PEN/PET blend and a portion of



**Figure 10** Change of the phase fractions with reaction time at 270°C for PEN/PEI (60/40) blend: ( $\bigcirc$ ) EIrich phase; ( $\triangle$ ) interfacial zone; ( $\square$ ) EN-rich phase.

them accumulate in the interfacial zone, because  $\chi_{\text{PEN/PET}}$  is greater than  $\chi_{\text{PEN/PET}}$ . Consequently, as transreactions proceed, the initial heterogeneous system comes to be a single phase through diminishing in composition difference between the EN- and EI-rich phases by diffusion of copolymers, together with the increase of interfacial fraction.

## CONCLUSION

Transreactions occurring between PEN and PEI polymers in the PEN/PEI blend were confirmed by <sup>1</sup>H NMR. The number-average sequence lengths and the degree of randomness were determined from the relative areas of proton peaks for three types of ethylene units. As the reaction time is prolonged, the number-average sequence lengths decrease, resulting in the increase of the randomness. The phase behavior during the transreactions was investigated by DSC. For the PEN/ PEI (60/40) blend samples heat treated at three different temperatures, the melting and coldcrystallization peaks fade away with reaction time, which is attributable to the disruption of the chain periodicity as a consequence of transreactions. In the early step of transreactions, two glass transitions reflecting the existence of two phases are observed and they approach mutually closer with reaction time. This shows that the composition difference in two coexisting phases decrease as the transreactions proceed. Irrespective of the reaction temperature, a single glass transition is observed when the randomness is greater than  $\approx 0.4$ . The weight fractions of two coexisting phases and interfacial zone were estimated by measuring the heat capacity changes at  $T_{\sigma}$  of the blends and the pure homopolymers. The interfacial fraction increases with the lapse of reaction time, resulting in the decrease of two coexisting phases. Therefore, it is considered that the homogenization of the PEN/PEI blend from the initial heterogeneous system to a single phase results from both the decrease of composition difference in two phases and the increase of interfacial fraction.

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